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IDENTIFICATION OF CARBAZOLE DERIVATIVES IN A HYDROTREATED COKER GAS OIL BY GAS CHROMATOGRAPHY AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY

I. IGNATIADIS
Département de Chimie, École Polytechnique, Route de Saclay, 91128 Palaiseau (France)
M. KUROKI
Department of Chemistry, Shibaura Institute of Technology, Fukasaku, Ohmiya-Shi, 330 Saitama (Japan)
and
P. J. ARPINO*
Département de Chimie, École Polytechnique, Route de Saclay, 91128 Palaiseau (France)
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SUMMARY

Non-basic nitrogen-containing polyaromatic hydrocarbons (NPAHs) were determined in a hydrotreated coker gas oil using gas chromatography and combined gas chromatography–mass spectrometry. The abundant NPAHs are alkylated benzologues of carbazole. The relative distribution of the carbazole derivatives in the sample is characterized by the presence of alkylcarbazoles with up to four carbon atoms in the substituents and alkylbenzocarbazoles branched by chains with two carbon atoms or less. Substances with polymethyl structures are the most abundant. Although severe hydrotreating conditions were applied to the feedstock, the observed NPAHs could not be eliminated. Their resistance is probably a function of the position of the alkyl groups on the aromatic nuclei.

INTRODUCTION

The investigation of nitrogen-containing polyaromatic hydrocarbons (NPAHs), mostly consisting of basic pyridine benzologues and non-basic pyrrole derivatives, that are present in crude oils and derived industrial fractions is becoming of great interest in many research programmes, *e.g.*, in oil refining, petroleum geochemistry and environmental impact studies.

The nitrogen abundance in crude oils is *ca.* 0.1–1.5% (w/w), depending on the origin of the sample. Despite this low abundance, nitrogen molecules are in general associated with adverse effects on fuel properties such as the colour and long-term stability during storage, as these molecules induce polymerization and precipitation of gum residues[1–5]. They are known poisons for acidic catalysts used in many oil upgrading processes such as cracking, reforming, isomerization, hydrodesulphurization and hydrodenitrogenation[6–8]. They are of concern in the environment as their

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incomplete combustion produces emission of toxic NO_x species in the urban atmosphere. Many aromatic congeners have shown mutagenic or carcinogenic activities in laboratory experiments[9–15], thus making their presence in oil-derived samples potentially dangerous. Finally, the organic geochemistry of these molecules is largely unknown; neither the natural precursors nor the evolution mechanisms during petroleum maturation have been clearly elucidated[16–21].

The catalytic removal of polyaromatic nitrogen molecules, a process called hydrodenitrogenation (HDN), is currently being investigated for the valorization of nitrogen-rich naphthas and gas oils to produce fractions that meet the accepted specifications of petrochemical bases and fuels for industrial and domestic applications.

It has been shown previously[22–26] that qualitative and quantitative investigations of a few selected NPAHs identified in a given feedstock and in the hydrotreated fractions contribute to a better understanding of hydrodenitrogenation mechanisms. The result can be extrapolated to conditions affecting other NPAHs in other feedstocks. However, the analytical investigation of NPAHs is difficult because they are present at trace levels in complex mixtures, with molecular weights covering a wide range (100–500 a.m.u.). Their low volatility and high polarity make GC investigations difficult. Finally, reference molecules are generally not available.

An analytical protocol combining several steps in series must be employed for the selective extraction, purification and identification of nitrogenous fractions. The complete identification of a molecule requires the establishment of the location of the nitrogen atom in the aromatic ring system and the nature and the location of alkyl substituents. Analytical methods used for these purposes include capillary column gas chromatography (GC), combined gas chromatography–mass spectrometry (GC–MS) and low-temperature fluorescence spectrometry.

Carbazole derivatives have been tentatively identified in crude oils and distillates[27–33], but the complete identification of individual molecules and detailed distribution patterns of homologous derivatives have seldom been reported. These objectives have been met in this laboratory[20,21,23,24,34], and in this study carbazole derivatives from a hydrotreated coker gas oil were selectively extracted and identified in order to investigate the substances that resist catalytic hydrotreatment under severe conditions of hydrogen pressure and temperature. The investigated sample is considered to be a typical example of materials that could be hydrotreated frequently in the future.

EXPERIMENTAL

Samples

The feedstock, denoted by F, was a light coker gas oil (160–350°C distillate) from the Veba-Öl refinery (Gelsenkirchen, F.R.G.) taken at the outlet of a delayed coker unit. This gas oil does not meet the specifications for direct use because of its excessive sulphur (3920 ppm) and nitrogen (570 ppm) contents. Hydrotreatment of F was performed in an experimental bench-scale unit of the continuous flow type (Catatest Unit, Géomécanique, under licence from the Institut Français du Pétrole). This unit was designed for the development of industrial catalysts. For the reaction, the catalyst was a mixture of NiO and MoO_3 on γ-alumina in the mass ratio 3:14:83. Different reaction mixtures (HDN1, HDN2, HDN3 and HDN4) were obtained, de-

pending on the hydrogenolysis conditions. HDN3 was selected for the study reported in this paper. Table I summarizes the operating conditions that led to the sample HDN3, and quantitative data from its elemental analysis. Carbazole derivatives comprise *ca.* 35–40% of total nitrogenous substances, the remaining fractions consisting mostly of basic pyridine benzologues.

Solvents and reagents

Solvents of pro analysi grade from Merck (Darmstadt, F.R.G.) or Carlo Erba (Milan, Italy) were glass-distilled prior to use. Adsorbents from Merck were silica (63–200 μm) and alumina (63–200 μm).

Selective removal of non-basic nitrogenous fractions

The analytical protocol was as described previously[23,34]. Carbazole derivatives were obtained in a single fraction, after five steps that successively eliminated basic nitrogen substances[35], carboxylic acids, saturated and aromatic hydrocarbons and weak acids. Separations were based on selective and reversible adsorption of a given class of substances on acid- or base-modified silica (SiO_2–HCl for basic fractions; SiO_2–KOH for the acids).

Capillary column GC and combined GC–MS

Glass capillary columns were prepared in the laboratory[36,37]. They were installed in a Perkin-Elmer Model Sigma 3 gas chromatograph equipped with a flame ionization detector or a Model 3920B gas chromatograph with parallel dual detection of column effluents using a flame ionization and a nitrogen-selective detector (NPD). A Varian Model 2700 gas chromatograph was coupled to a DuPont Model 21-492B mass spectrometer for GC–MS. A DuPont Model 094B-2 data system was used for data acquisition and processing.

Carbazole derivatives were classified according to their Z number derived from the molecular weight, obtained by GC–MS, using the general formula $C_nH_{2n+z}N$.

Identification of individual substances was based on the comparison of mass spectra and on capillary column co-elution of substances and standards on three stationary phases.

Derivatization by permethylation

Permethylation of carbazole fractions was carried out as described previously[34]. The method was a test for the presence of carbazoles in the final mixture, and it helped to locate non-reacting substances, including polar non-nitrogenous molecules and contaminants (phthalates). In addition, the less polar N-methylcarbazoles were more readily amenable to GC and GC–MS investigations.

Reference compounds

Carbazole was obtained from Merck. Methyl-, dimethyl- and trimethylcarbazoles were synthesized in the laboratory in Japan[38,39]. Benzocarbazoles were gifts from Dr. Perin (Institut Curie, Orsay, France).

TABLE I

OPERATING CONDITIONS AND QUANTITATIVE RESULTS FROM ELEMENTAL ANALYSIS FOR THE HYDROTREATED SAMPLE HDN3

VVH = Volume per volume per hour.

Sample	*Operating conditions*				*Sulphur*		*Nitrogen*	
	Temperature (°C)	*Hydrogen pressure (bar)*	*VVH (h^{-1})*	*Catalyst*	*S content* (ppm)*	*HDS removal** (%)*	*N content* (ppm)*	*HDN removal** (%)*
F	–	–	–	–	3920	–	570	–
HDN3	360	70	4	$NiO–MoO_3–Al_2O_3$	549	86	180	68

* From elemental analysis.

** From the equation $HDS(\%) = \frac{S_F - S_{HDN3}}{S_F} \cdot 100$ and $HDN(\%) = \frac{N_F - N_{HDN3}}{N_F} \cdot 100$.

RESULTS AND DISCUSSION

The ring numbering of the carbazole derivatives used is illustrated in Fig. 1.

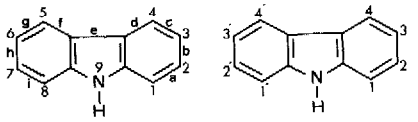

Fig. 1. Structures and ring numbering of carbazole derivatives.

GC retention parameters

In a previous study[38], empirical rules were deduced for predicting the elution order of carbazole, a series of methylcarbazoles and dimethylcarbazoles, when separated on three different stationary phases. For instance, the elution order for methylcarbazoles was found to be 1-MC < 3-MC < 2-MC < 4-MC, where MC represents methylcarbazole. The relationship can be written more concisely as $1 < 3 < 2 < 4$ or $1' < 3' < 2' < 4'$, and for symmetrical dimethylcarbazoles $1,1' < 3,3' < 2,2' < 4,4'$. Hence the elution order of monomethylcarbazoles is not altered significantly when a second methyl group is introduced into the molecule symmetrically with respect to the nitrogen atom. More generally, the elution order $1 < 3 < 2 < 4$ is valid for asymmetric dimethylcarbazoles, with only a few exceptions[40].

In this study, the retention indices of twelve trimethylcarbazoles (among the 28 possible isomers) were measured on OV-73 and OV-1701 stationary phases (Table II). The elution orders follow the same trends as those observed for the lower homologues. In particular, the elution order $1 < 3 < 2 < 4$ is observed for the following

TABLE II

RETENTION INDICES (MEANS OF TWO MEASUREMENTS) FOR THE 12 TRIMETHYLCARBAZOLES (AMONG THE 28 POSSIBLE ISOMERS) MEASURED ON OV-73 AND OV-1701 STATIONARY PHASES

OV-73 = 5.5% phenyl, 94.5% methylsilicone; OV-1701 = 25% cyanopropyl, 7% phenyl, 86% methylsilicone.

Trimethylcarbazole	*OV-73 (t_{isoth} = 190°C; glass capillary column, 85 m × 0.3 mm I.D.)*	*OV-1701 (t_{isoth} = 200°C; glass capillary column, 45 m × 0.28 mm I.D.)*
1,4,8-	2129.4	2385.7
1,4,6-	2160.2	2425.1
1,5,7-	2170.6	2432.7
1,4,7-	2171.6	2428.9
2,4,6-	2186.8	2445.6
2,4,7-	2200.0	2456.5
1,3,4-	2200.0	2468.6
2,3,6-	2217.0	2478.3
1,4,5-	2222.4	2493.8
3,4,6-	2223.8	2486.2
2,3,5-	2227.2	2483.3
2,4,5-	2248.0	2516.4

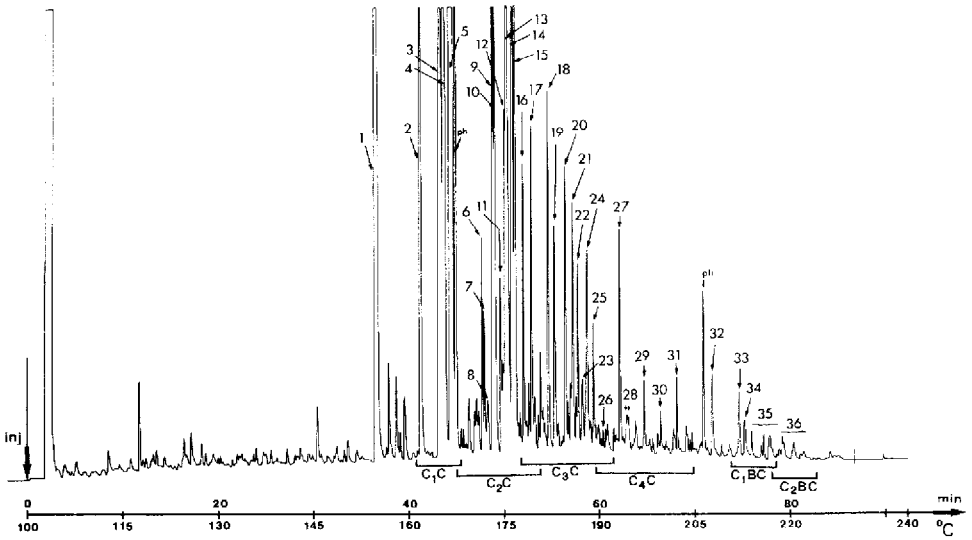

Fig. 2. Gas chromatogram of the non-basic fraction (carbazole derivatives) extracted from the hydrotreated sample HDN3. GC conditions: glass capillary column coated with OV-73, 68 m × 0.28 mm I.D., 0.15 μm film thickness, temperature programmed from 100 to 200°C at 1.5°C/min. For peak identification, see Table III. C_xC = x-alkylcarbazole; C_xBC = x-alkylbenzocarbazole; ph = phthalate.

series: 1,4,8- < 1,4,6- < 1,4,7- < 1,4,5- or 1,4,1′- < 1,4,3′- < 1,4,2′- < 1,4,4′-; 2,4,8- < 2,4,6- < 2,4,7- < 2,4,5- or 2,4,1′- < 2,4,3′- < 2,4,2′- < 2,4,4′-; 1,4,8- < 2,4,8-; 2,3,6- < 2,3,5- < 2,4,5-; and 1,3,4- < 3,4,6-.

Identification of carbazole derivatives in HDN3

An example of the GC analysis of the hydrotreated fraction HDN3 is presented in Fig. 2. The substances identified in this mixture are listed in Table III. Computer-generated ion current traces for masses corresponding to the molecular weight of carbazole (m/z 167) and its higher homologues (m/z 181, 195, 209) are presented in Fig. 3. The ordinate is the relative intensity expressed as a percentage of the maximum abundance of 4-methylcarbazole (taken as 100) in the mass chromatogram for m/z = 181.

Several hydrocarbons with no nitrogen atoms are still present among the early eluting peaks. They correspond to substances that could not be eliminated by the extraction procedure and to phthalates (denoted by ph in Fig. 2), presumably introduced during the work-up.

Several substances have been declared "absent" when a specific investigation of the target molecule was unsuccessful, given the detection limit of the protocol adopted in this study.

Identified non-basic NPAH present in HDN3 consist exclusively of polyalkylbenzologues of carbazole with three or four aromatic rings and one, two or three methyl substituents. Molecular weights range from 167 ($C_{12}H_9N$, carbazole) to 235 ($C_{18}H_{15}N$, C_2-benzocarbazoles). Dominant substances are triaromatic derivatives in the series $C_nH_{2n-15}N$. Carbazole and its polyalkylated benzologues present in HDN3

TABLE III

CARBAZOLE DERIVATIVES IDENTIFIED IN THE HYDROTREATED SAMPLE HDN3

For compound identification, see Figs. 2 and 3.

No. of peak	*Z*	*MW*	*Empirical formula*	*Structure*	*Identification methods*
1	−15	167	$C_{12}H_9N$	Carbazole	GC, GC–MS
2	−15	181	$C_{13}H_{11}N$	1-Methylcarbazole	GC, GC–MS
3	−15	181	$C_{13}H_{11}N$	3-Methylcarbazole	GC, GC–MS
4	−15	181	$C_{13}H_{11}N$	2-Methylcarbazole	GC, GC–MS
5	−15	181	$C_{13}N_{11}N$	4-Methylcarbazole	GC, GC–MS
6	−15	195	$C_{14}H_{13}N$	1,3-Dimethylcarbazole	GC, GC–MS
7	−15	195	$C_{14}H_{13}N$	1,6-Dimethylcarbazole	GC, GC–MS
8	−15	195	$C_{14}H_{13}N$	1,7-Dimethylcarbazole	GC, GC–MS
9	−15	195	$C_{14}H_{13}N$	1,4-Dimethylcarbazole	GC, GC–MS
10	−15	195	$C_{14}H_{13}N$	1,5-Dimethylcarbazole	GC, GC–MS
11	−15	195	$C_{14}H_{13}N$	3,6-Dimethylcarbazole	GC, GC–MS
12	−15	195	$C_{14}H_{13}N$	2,6-Dimethylcarbazole	GC, GC–MS
13	−15	195	$C_{14}H_{13}N$	2,7-Dimethylcarbazole	GC, GC–MS
				1,2-Dimethylcarbazole	GC, GC–MS
				3,5-Dimethylcarbazole	GC, GC–MS
14	−15	195	$C_{14}H_{13}N$	2,4-Dimethylcarbazole	GC, GC–MS
15	−15	195	$C_{14}H_{13}N$	2,5-Dimethylcarbazole	GC, GC–MS
16	−15	195	$C_{14}H_{13}N$	2,3-Dimethylcarbazole	GC, GC–MS
17	−15	195	$C_{14}H_{13}N$	3,4-Dimethylcarbazole	GC, GC–MS
18	−15	209	$C_{15}H_{15}N$	1,4,6-Trimethylcarbazole	GC, GC–MS
19	−15	209	$C_{15}H_{15}N$	1,4,7-Trimethylcarbazole	GC, GC–MS
				1,5,7-Trimethylcarbazole	GC, GC–MS
20	−15	209	$C_{15}H_{15}N$	2,4,6-Trimethylcarbazole	GC, GC–MS
21	−15	209	$C_{15}H_{15}N$	2,4,7-Trimethylcarbazole	GC, GC–MS
22	−15	209	$C_{15}H_{15}N$	1,3,4-Trimethylcarbazole	GC, GC–MS
23	−15	209	$C_{15}H_{15}N$	1,4,5-Trimethylcarbazole	GC, GC–MS
24	−15	209	$C_{15}H_{15}N$	3,4,6-Trimethylcarbazole	GC, GC–MS
25	−15	209	$C_{15}H_{15}N$	C_3-Alkylcarbazole	GC–MS
26	−15	209	$C_{15}H_{15}N$	2,4,5-Trimethylcarbazole	GC, GC–MS
27 at 31	−15	223	$C_{16}H_{17}N$	C_4-Alkylcarbazoles	GC–MS
32	−21	217	$C_{16}H_{11}N$	Benzo[*a*]carbazole	GC, GC–MS
33	−21	231	$C_{17}H_{13}N$	Methylbenzocarbazole	GC–MS
34	−21	217	$C_{16}H_{11}N$	Benzo[*c*]carbazole	GC, GC–MS
35	−21	231	$C_{17}H_{13}N$	Methylbenzocarbazoles	GC–MS
36	−21	245	$C_{18}H_{15}N$	C_2-alkylbenzocarbazoles	GC–MS

are known constituents of most cude oils, but they are even more abundant in hydrotreated samples compared with other substances.

Triaromatic compounds

Twenty-six substances (peaks 1–25) were identified. Alkyl substituents are nearly exclusively methyl groups. The maximum number of methyl groups is 3. Longer chains were rare or absent. This is surprizing as the number of theoretical possible isomers is high: 4 C_1-carbazoles, 20 C_2-carbazoles (16 dimethyl- and 4 ethyl-) and 64 C_3-carbazoles (28 trimethyl-, etc.).

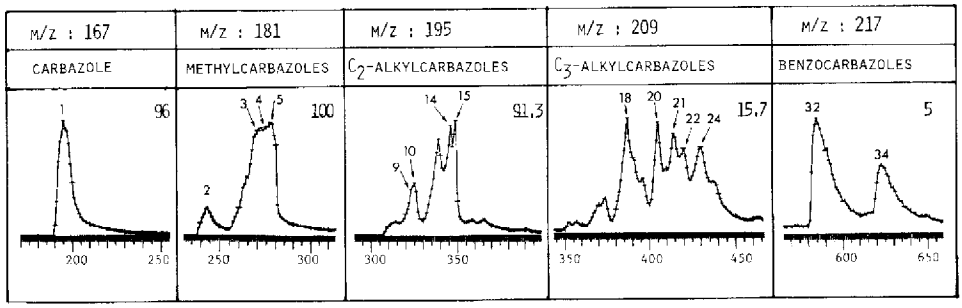

Fig. 3. Computer-generated ion current traces for masses corresponding to the molecular weight of carbazole (m/z 167), its alkyl derivatives (m/z 181, 195, 209) and higher homologues, benzocarbazoles (m/z 217). The ordinate is the relative intensity expressed as a percentage of the maximum abundance of 4-methylcarbazole in the mass chromatogram for m/z = 181. GC conditions: glass capillary column coated with OV-73, 50 m × 0.3 mm I.D., 0.20 μm film thickness, temperature programmed from 150 to 260°C at 2°C/min. For peak identification, see Table III.

Target research of the following carbazole derivatives failed to produce any significant identification:

C_2-	C_3-	C_4-
ethyl-	ethyl,methyl-	ethyl,ethyl-
	propyl-	propyl,methyl-
	isopropyl-	isopropyl,methyl-
		butyl-
		isobutyl-

Among the abundant polymethylcarbazoles present in HDN3, many bear a methyl group at C-4, for instances:

4-methyl-	1,4*-dimethyl-	1,4,5-trimethyl-
	2,4-**	1,4,6-**
	3,4-*	1,4,7-
		2,4,5-
		2,4,6-*
		2,4,7-
		1,3,4-
		3,4,6-*

(abundant peaks are indicated by one asterisk and the prominent peaks in the series by two asterisks).

Studies of carbazole isomers, including benzoindoles and naphthopyrroles, and their alkyl homologues, gave no evidence of any significant presence.

Tetraaromatic compounds

Benzo[*a*]carbazole (peak 32) and benzo[*c*]carbazole (peak 34) are present, whereas benzo[*b*]carbazole is absent. They produce the ion current profile for m/z

217 shown in Fig. 3. On the other hand, target research of benzocarbazole isomers, including naphthoindoles, anthrapyrroles and phenanthropyrroles, failed to produce any positive identification.

Alkyl homologues, again with the presence of abundant polymethyl derivatives, were suspected, but full identification was not possible as reference compounds were not available. Higher benzologues with more than four aromatic rings were not detected in HDN3.

CONCLUSION

Lack of significance of non-basic NPAHs in HDN3

As frequently observed, the chemical structure of the abundant carbazole derivatives in HDN3 are non-specific and similar to those identified in most crude oils and other hydrotreated feedstocks. However, differences in the relative abundances are noticeable: in the six crude oils, of different origins and different geological history, studied in this laboratory for their carbazole contents[20], alkylbenzocarbazoles were the major compounds, whereas alkylcarbazoles were rare. The reverse situation is observed in this study for HDN3, where alkylcarbazoles are the dominant substances.

Effects of the hydrotreatment on the feedstock

Only 68% of the nitrogen content of F was removed by the process. The remaining nitrogen atoms are mostly located in basic NPAH with azaarene or alkylaniline structures, amounting to 19% of the remaining nitrogen content. Non-basic NPAHs of the carbazole family account for the remainder of the unreacted nitrogen atoms, *i.e.*, 13%.

It appears that the presence of a methyl group at C-4 (or C-5, *i.e.*, C-4') could dramatically reduce the reactivity of the molecule towards a catalytic hydrotreatment, or reducing conditions during petroleum maturation, causing a preferential accumulation of these derivatives relative to the other isomers.

The results confirm previous studies that had indicated the general resistance of carbazole derivatives towards severe hydrotreatment conditions[22,24]. Differences in reactivity among isomers may exist, causing the preferential accumulation of the most stable isomers. The reason for the specific increased resistance of some non-basic NPAHs is probably linked to the position of the alkyl substituents on the aromatic nuclei. This fact was also observed previously with azaarenes from crude oils and hydrotreated fractions.

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